Spectrophotometric determination of ferbam (iron(III) dimethyldithiocarbamate) in a commercial sample and wheat grains using 4,7-diphenyl-1,10-phenanthroline

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Abstract: A procedure has been developed for the determination of iron(III) dimethyldithiocarbamate by converting it into iron(III)- bathophenanthroline complex, which is then dissolved in water in the presence of sodium dodecyl sulphate as a surfactant, and the absorbance measured at 532 nm against a reagent blank. Beer's law is obeyed over the concentration range 0.3–20 μg ml^{-1} in the final solution. The method is sensitive, highly selective and can be used for the determination of ferbam in a commercial sample, in mixtures with various dithiocarbamates (ziram, zineb, maneb, etc.) and from wheat grains.

Keywords: spectrophotometry; ferbam; commercial sample; bathophenanthroline

1 INTRODUCTION

Ferbam (iron(III) dimethyldithiocarbamate) is a well-known dithiocarbamate fungicide widely used against a variety of plant pathogenic fungi. Several methods are currently available in the published literature for the determination of dithiocarbamate fungicides. In one such method ferbam is determined on the basis of its decomposition by hot mineral acids to amine and carbon disulphide. This is then absorbed in methanolic potassium hydroxide solution and the potassium methyl xanthate thus formed is titrated iodometrically.[1] In another approach, carbon disulfide is absorbed in an ethanol solution containing copper(II) and an alkylamine to form copper dialkyldithiocarbamate, which can be determined photometrically.[2–4] Dithiocarbamates have also been determined in vegetable foodstuffs using high-performance liquid chromatography,[5] extraction voltammetry[6] and titrimetry.[7] Ferbam is also determined by converting it into molybdenum,[8] copper[9] and phenanthroline[10] complexes. The extraction of the molybdenum complex is slow and requires about five minutes of shaking; the method using copper involves complexation in acid medium and the method with 1,10-phenanthroline involves adsorption onto microcrystalline naphthalene, in which the separation and dissolution of the complex is quite tedious. The present method is direct and does not involve extraction. Dithiocarbamates can also be determined by methods which the do not involve acid decomposition; these include iodometry in anhydrous solvents,[11,12] indirect titration with EDTA,[13] polarography[14] and determination of the metallic component of the pesticide using different methods.[15,16] McLeod and McCulley[17] determined dithiocarbamate fungicides by head-space gas chromatography of the carbon disulfide evolved in controlled conditions from foodstuffs, and similar methods were also given by the Committee for Analytical Methods.[18] However, all these methods suffer from the following disadvantages:

(a) Methods other than gas chromatography are indirect, time-consuming and sensitivity is low.
(b) Gas chromatographic methods are sensitive but suffer from lack of selectivity, since all dithiocarbamate pesticides evolve carbon disulfide on acid hydrolysis.

Here we present a relatively simple, rapid, sensitive and selective spectrophotometric method involving the conversion of ferbam into an iron(III) bathophenanthroline complex. Ferbam reacts with bathophenanthroline to form a red complex which is suitable for spectrophotometric determination. The reaction between ferbam and bathophenanthroline

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Table 1. Determination of ferbam from fortified samples of wheat grains

Crop[a]	Fortification μg	Fortification ($\mu g\,g^{-1}$)	Found by present method (μg)	RSD (%)	Found by Rangaswamy et al[9] method (μg)	RSD (%)
Wheat	10	0.5	9.5	2.3	9.4	2.4
	50	2.5	49.5	2.1	49.3	2.2
	100	5.0	99.6	1.9	99.5	2.0
	150	7.5	146.8	1.4	145.3	1.6

[a] Amount of crop = 20 g; Each result is average of 10 experiments.

may be shown as:

$$\mathrm{Iron(DMDTC)_3 + BPHEN} \rightarrow \mathrm{Iron(BPHEN)_3^{3+} + 3\ DMDTC}$$

where DMDTC = dimethyldithiocarbamate and BPHEN = 4,7-diphenyl-1,10-phenanthroline

2 EXPERIMENTAL

2.1 Equipment and reagents

A digital pH meter and a Varian Cary 2400 spectrophotometer was used. Ferbam was obtained from Riedel-de Haën (Pestanal®) and used as such. A stock solution of pure (100%) ferbam (1 g litre^{-1}) was prepared by dissolving 100 mg of this reference material in 100 ml of acetonitrile and further diluting the resultant solutions with acetonitrile as desired. Solutions of 4,7-diphenyl-1,10-phenanthroline (bathophenanthroline; Merck, GR; 1 g litre^{-1}), sodium dodecyl sulphate (SDS; Merck, GR; 20 g litre^{-1}) and of hydroxylamine hydrochloride (Merck, GR; 100 g litre^{-1}) were prepared in distilled water. Acetate buffer was prepared in distilled water by dissolving sodium acetate trihydrate (Merck GR; 68 g) in water (400 ml) and adjusting the pH to 4.5 by adding glacial acetic acid (Merck, GR 25–30 ml) and making up the total volume to 500 ml.

Stock solution of various salts were prepared by dissolving them in water. Nabam, ziram, maneb and thiram were obtained from Riedel-de Haën (Pestanal®). Solutions of the dithiocarbamates were prepared by dissolving them in distilled water or in the organic solvents given in parentheses: ziram and thiram (acetonitrile, Merck) and zineb and maneb (dimethylsulfoxide, Merck). Synthetic samples were prepared by mixing the solutions of the constituents to give the required composition.

2.2 Procedures

2.2.1 Preparation of the calibration curve

To known volumes of sample solutions containing 3.0–200 μg of ferbam in a 10-ml standard flask were added bathophenanthroline solution (1.5 ml), hydroxylamine hydrochloride (1.5 ml), aqueous acetate buffer solution (1.5 ml, pH = 4.5) and SDS (1 ml) and the volume was made up to 10 ml with distilled water. The mixture was shaken and allowed to stand for 5 min; the absorbance of each solution was then measured at 532 nm against a reagent blank prepared under similar conditions, and plotted against ferbam concentration.

2.2.2 Determination of ferbam from fortified samples of wheat grains

The method was applied for the determination of ferbam from fortified samples of wheat grains. A known amount of ferbam in acetonitrile was crushed with 20 g of wheat grains with pestle and mortar and shaken mechanically with chloroform (100 ml) for 1 h. The mixture was filtered and the residue in the funnel was washed with chloroform (3 × 10 ml). The extracts were evaporated to 2.0 ml on a water bath (70–90 °C) and the remaining solvent was removed in a current of dry air at room temperature. The residue was dissolved in acetronitrile and determined by the general procedure. Untreated samples were taken as reference and the results indicated good recoveries in all cases. The results of the determinations are given in Table 1.

2.2.3 Analysis of a commercial sample

The method was applied for the determination of ferbam in a commercial sample of a 750 g kg^{-1} Ferbam WP. A solution of the formulated product was prepared as described Section 2 and determined by the general procedure. The results obtained by the present method were compared with those obtained by the Rangaswamy *et al*[8] method in which ferbam was

Table 2. Determination of ferbam in a commercial sample[a]

Source	Present (μg)	Found by present method (μg)	RSD (%)	Found by Rangaswamy et al[9] method (μg)	RSD (%)
Ferbam	10	9.9	1.8	9.9	2.2
(750 g kg^{-1} W P)	50	49.9	1.6	49.8	2.1
	100	99.4	1.4	96.2	1.9
	160	158.8	1.2	157.9	1.6
	180	179.5	0.9	178.6	1.3

[a] Each result is a mean of 10 experiments.

Table 3. Determination of ferbam in synthetic mixtures[a]

Sample no	Composition and percentage	Amount of ferbam (μg) Taken	Found	RSD (%)
1	Ferbam: 50 Ziram: 50	40.0	40.2	1.23
2	Ferbam: 50 Thiram: 50	40.0	39.9	0.84
3[b]	Ferbam: 11.76 Maneb: 76.48 Zineb: 11.76	20.0	20.2	1.4

[a] Each result is average of 10 experiments.
[b] This composition is identical to the active ingredient ratio in the Pennwalt product (ferbam 10%, maneb 65% and zineb 10%).

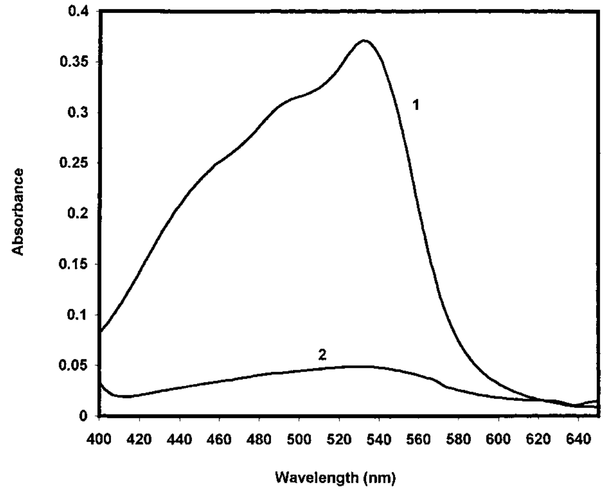

Figure 1. Absorption spectra of (1) ferbam as iron(III)-bathophenanthroline complex in SDS; (2) ferbam in acetonitrile; reference reagent blank. Ferbam 50 μg; bathophenathroline 1.5 ml (1 g litre^{-1}), hydroxylamine hydrochloride 1.5 ml (100 g litre^{-1}); SDS 1.0 ml (20 g litre^{-1}); acetate buffer 1.5 ml (pH = 4.5).

determined colorimetrically after reaction with cuprous chloride in 0.3 M hydrochloric acid to form a yellow copper complex and measuring the absorbance at 385 nm. The results of the determinations are given in Table 2.

2.2.4 Determination of ferbam in synthetic mixtures

Aliquots of the samples were prepared by mixing solutions of ferbam with other dithiocarbamate solutions which were then analysed by the general procedure. The results of the determinations are given in Table 3.

3 RESULTS AND DISCUSSION

3.1 Absorption spectra

The absorption spectrum of the complex of ferbam with bathophenanthroline in the presence of SDS was recorded against a reagent blank. The complex shows an absorption maximum at 532 nm (Fig 1), so this wavelength was selected for all further measurements.

3.2 Effect of standing time

It was observed that the absorbance of the solution became constant after 2–3 min, so, for all the measurements, 5 min standing time was selected. The absorbance of the complex remained practically constant for more than 24 h.

3.3 Beer's law and sensitivity

Under the conditions described above a calibration graph for the determination of ferbam was linear over the concentration range 0.3–20 μg ml^{-1} (Fig 2) of the final solution. Aliquots containing 50 μg (5 μg ml^{-1}) were taken from the standard reference solution and analysed by the general procedure. Ten replicate determinations on these sample solutions of ferbam gave a mean absorbance of 0.37 with a relative standard deviation of ±0.93%. The molar absorptivity ($\varepsilon = A/Lc$; where ε is the molar absorptivity coefficient–the value of absorbance for 1 M concentration of a solute, and L is the optical path length) was calculated to be 3.12×10^4 l mol^{-1} cm^{-1}, and Sandel's sensitivity,[19] which represents the number of micrograms of the determinand per 10 ml of the final solution having an absorbance of 0.001 for a path length of 1 cm, was found to be 0.013 μg cm^{-2}.

3.4 Interference

Sample solutions (10 ml) containing 50 μg of ferbam and various amounts of different alkali metal salts or metal ions were prepared and the general procedure was applied. For the following foreign anions, 20 mg did not interfere in the determination of ferbam: bromide, acetate, chloride, nitrate, sulfate and oxalate. Of the following metal ions examined, 0.20 mg did not interfere in the determination of ferbam: Pb(II), Zn(II), Cu(II) and Bi(III). Fe(II) or Fe(III) if present with ferbam interfere in the determination of ferbam. However, their interference can be avoided by the pre-extraction of ferbam into chloroform; Fe(II) and

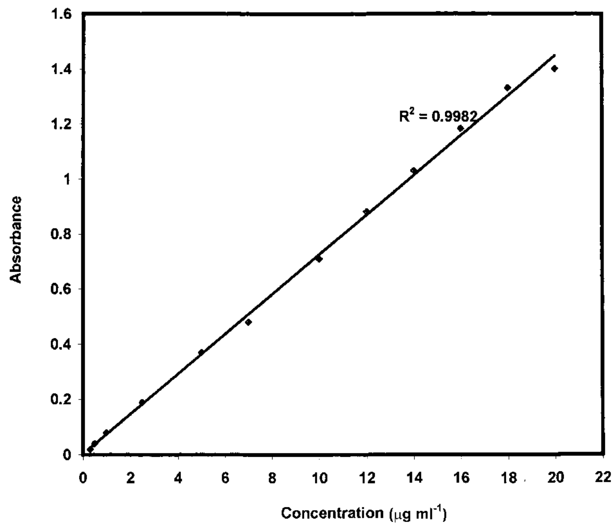

Figure 2. Calibration curve for the determination of ferbam λ_{max} 532 nm. Rest of the conditions the same as in Fig 1.

Table 4. Comparison of molar absorptivity with earlier methods

Molar absorptivity ($l\ mol^{-1} cm^{-1}$)	*Method*	*Remark*	*Reference*
1.33×10^4	Molybdenum	Requires acidic medium (2 M H_2SO_4) and equilibrium time 5 min	8
1.46×10^4	Selenite	Other dithiocarbamates interfere	20
5.3×10^4	Diphenylcarbazone	Maneb, zineb, ziram interference can be avoided using only masking agents	21
1.2×10^4	1,10-phenanthroline	Requires adsorption of the complex onto naphthalene, which is tedious and time-consuming	10
3.12×10^4	Bathophenanthroline + SDS[a]	More selective and sensitive	This work

[a] SDS: Sodium dodecyl sulphate.

Fe(III) will remain in the aqueous phase and ferbam can be determined by the general procedure after evaporation of the chloroform to dryness. Interference due to other dithiocarbamates such as disodium ethylenebisdithiocarbamate (nabam), manganese ethylenebisdithiocarbamate (maneb), zinc ethylenebisdithiocarbamate (zineb), tetramethylthiuramdisulfide (thiram) and sodium diethyldithiocarbamate were studied and found not to interfere in the determination of ferbam. As untreated samples are taken for reference, any interference due to organic iron complexes is eliminated.

4 COMPARISON OF SENSITIVITY

The present method is more selective than the earlier spectrophotometric methods as it permits safely the determination of ferbam in the presence of nabam, ziram, maneb, zineb, vapam, dibam and sodium diethyldithiocarbamate without any interference, whereas this is not possible using the earlier reported methods. A comparison of the molar absorptivity with other methods is given in Table 4. The present method is more sensitive than the carbon disulfide evolution methods, as according to Lowen[3] the minimum of evolved carbon disulphide is 10 µg. According to Cullen[4] and many others a minimum of 20 µg of carbon disulfide evolution is required for the determination, but according to the present method a minimum of 3 µg of ferbam, equivalent to 1.64 µg of evolved carbon disulfide can be determined. The wide applicability, simplicity and selectivity of this method make it preferable to others.

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REFERENCES

1 Clarke DG, Baum H, Stanley EL and Hester WE, Determination of dithiocarbamates. *Anal Chem* **23**:1842–1846 (1951).
2 Simpson BW, Determination of dithiocarbamates in carbonate-based formulations of maneb and zineb, *Pestic Sci* **2**:127–128 (1971).
3 Lowen WK, Determination of dithiocarbamate residues on food crops. *Anal Chem* **23**:1846–1850 (1961).
4 Cullen TE, Spectrophotometric determination of dithiocarbamate residues on food crops. *Anal Chem* **36**:221–224 (1964).
5 Gustafsson KH and Falhgren CH, Determination of dithiocarbamate fungicides in vegetable foodstuffs by high performance liquid chromatography. *J Agric Food Chem* **31**:461–463 (1983).
6 Ulakhovich NA, Medyantseva ED, Frolova VF and Romanova ON, Application of catalytic currents of hydrogen for complexes of metals with sulphur-containing ligands in extraction voltammetry. *Zh Anal Khim* **38**:1963–1968 (1983).
7 Verma BC, Sidhu HS and Sood RK, Determination of thiuram disulfide and analysis of thiuram disulfide-dithiocarbamate mixtures. *Talanta* **29**:703–705 (1982).
8 Rao AL and Verma N, Determination of ferbam (ferric dimethyldithiocarbamates) residues in apples by a spectrophotometric method. *J Indian Acad For Sci* **24**:1–5 (1985).
9 Rangaswamy JR, Poornima P and Majumder SK, Rapid colorimetric method for estimation of ferbam and ziram residues on grains. *J Assoc Off Anal Chem* **53**:1043–1044 (1970).
10 Malik AK and Rao ALJ, Spectrophotometric determination of iron(III) dimethyldithiocarbamate. *Talanta* **44**:177–183 (1997).
11 Grand AF and Tamres M, Titration of some metal diethyldithiocarbamate by iodine in chloroform. *Anal Chem* **40**:1904–1905 (1968).
12 Clyde DD, Determination of xanthates, dithiocarbamates and some fungicides by titration with electrogenerated iodine in anhydrous acetonitrile. *J Assoc Off Anal Chem* **66**:646–650 (1983).
13 Hyman AS, A rapid method for the determination of manganese in maneb and its formulations. *Analyst* **94**:152–153 (1969).
14 Halls DJ, Townshend A and Zumen P, The polarographic determination of trace dithiocarbamates and their heavy metal complexes. *Analyst* **93**:219–223 (1968).
15 Quintero MC, Silva M and Perez-Bendito D, Kinetic determination of zineb in agricultural samples by continuous addition of reagent. *Talanta* **38**:359–363 (1991).
16 Perez-Ruiz T, Martinez-Lozano C, Tomás V and Casajús R, Flow injection fluorimetric determination of nabam and metham. *Talanta* **43**:193–198 (1996).
17 McLeod HA and McCully KA, Head space gas procedure for screening food samples for dithiocarbamate pesticide residues. *J Assoc Off Anal Chem* **52**:1226–1230 (1969).
18 Panel on Determination of Dithiocarbamates Residues of the Committee for Analytical Methods for Residues of Pesticides and Veterinary Products in Foodstuffs of the Ministry Agriculture, Fisheries and Foods, Determination of residues of dithiocarbamate pesticides in foodstuffs by a headspace method. *Analyst* **106**:782–787 (1981).
19 Sandell EB, *Colorimetric Determination of Traces of Metals*, 3rd edn, Interscience publishers, New York. p 82 (1959).
20 Malik AK Rao ALJ and Puri BK, Spectrophotometric determination of ferbam using sodium selenite. *Intern J Environ Anal Chem* **44**:159–166 (1991).
21 Malik AK and Rao ALJ, Spectrophotometric determination of ziram, ferbam and zineb using diphenylcarbazone. *Talanta* **8**:941–944 (1991).